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JANUARY 27, 1965

E. F. HOUGHTON & CO.

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WATER BASED HYDRAULIC FLUIDS

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ABSTRACT

During this period, emphasis has been centered on improving the corrosion properties of our candidate fire resistant, water based hydraulic fluid, A series of hydroxy alkylene carboxylates have been prepared as potential corrosion inhibitors. In addition, a continuing study has been made of the correlation existing between corrosion of control panels in hydraulic systems and bench corrosion tests.

Several aromatic ether derivatives are concurrently being evaluated as autoignition improvers. An attempt has also been made to alter the structure of the glycol portion of our candidate fluid so that a higher autoignition temperature is attained in the finished formula.

INTRODUCTION

Protecting galvanized metal surfaces against corrosive attack by our candidate hydraulic fluid during pump operation has been studied with the belief that sea water contamination will present additional problems. In preliminary bench corrosion tests, a small percentage of an aromatic alkylene carboxylate markedly inhibited zinc corrosion.

In most cases, inorganic inhibitors tested caused a great deal of wear to the ring and vanes of the Vickers hydraulic pump.

The flash and fire point determinations of "dehydrated" fluids have been markedly affected by crystallization of inhibitors. A salt cake builds up around the thermometer affecting the accuracy of the thermometer. The use of Pensky-Martens equipment may overcome this problem observed with the Cleveland Open Cup equipment.

Synthesis of Corrosion and Ignition Inhibitors

Bench tests have indicated a need for corrosion inhibitors which will not crystallize from solution or cause excessive wear to pump parts during hydraulic operation. Several materials have been prepared to overcome this problem which are essentially aromatic carboxylates having alkylene groups of different chain lengths. These fluids are coded HPB, HDEB and HTEB. Their physical properties are listed in Appendix Table I. Preliminary corrosion studies have shown that HTEB does inhibit zinc corrosion when used as an additive to the glycol hydraulic fluid. Pertinent data are shown on page 3 in comparison with our prototype fluid.

Stirring Corrosion Test @ 140°F

(Modified Turbine Oil Rust Test outlined in the Appendix under Test Procedure)

Fluid	Test Specimen (1"x2"x¼")	Weight Change	Appearance
Base A (Prototype Fluid)	Zinc	-41.0 mg	Dull, gray film Several black stains
Base A + 1.0% HTEB	Zinc	-11.0 mg	Clean

Dynamic Corrosion Test

(Conducted in the reservoir of the vane pump of the hydraulic circuit - See Appendix under Test Procedures)

Test Fluid	Metal Specimens Wt. Change and Appearance					
	Zinc	Steel	Aluminum	Brass	Bronze	Copper
Base A	-30.1 mg	-0.4 mg	-0.1 mg	-0.9 mg	-0.3 mg	-0.6 mg
	White chalking and pitting	Clean and bright	Clean and bright	Clean and bright	Light stain	Clean and bright
Base A + 1.0% HTEB	- 4.9 mg	-6.2 mg	+0.7 mg	-0.4 mg	+0.3 mg	+0.4 mg
	White film	Dark stain	Bright	Slight stain	Slight stain	Bright

Synthesis has also been directed towards forming new materials which would increase the autoignition temperature of our proposed hydraulic fluid candidate. Several candidates show promise for this purpose. The data summarized below tabulate the AIT results obtained when two aromatic ether derivatives designated HPPE and HPMPE, and a phenol-formaldehyde resol type coded PF-450 are added in 10 percent concentration to a water based, hydraulic fluid test formula.

Test Formula

Polyglycol c	20.0%
Additive	10.0%
Polyglycol b	34.0%
Water	36.0%

Additive	Autoignition Temperature
None	820°F
HPPE	850°F
HPMPE	860°F
PF-450	870°F

Further, an attempt was made to alter the glycol portion of the proposed prototype hydraulic fluid by a condensation reaction using epichlorohydrin. The autoignition temperature increased only when the treated material was dissolved in water. This effect is shown below.

Material	Autoignition Temperature
Polyglycol b	780°F
Treated Polyglycol b	775°F
40% Polyglycol b 60% Water	835°F
40% Treated Polyglycol b 60% Water	870°F

Whtn the treated polyglycol b was used as a replacement for the polyglycol b in a fully compounded hydraulic fluid formula, the autoignition temperature was not appreciably raised.

Flash and Fire Point Investigations

An apparent lowering of the flash and fire points of several water based hydraulic fluid formulas has been previously reported in the presence of 0.5 percent of sodium benzoate. An analysis of the procedure led to the conclusion that some inhibitors salt out of the dehydrated solution and form a cake on the surface prior to the ignition test. Caking increases until the last traces of water are removed from the fluid, during the heating process, in the flash cup. Solids collect around the immersed thermometer bulb, insulating it. The temperature observed is, therefore, considerably lower than the main body of the fluid. Flash and fire points recorded are erroneous due to this condition.

To obtain true ignition test results, the test fluid must be continuously mixed to disperse any solids collecting around the thermometer. In the Cleveland Open Cup, higher flash and fire points are obtained by this method.

Ideally, we should use liquid inhibitors, which do not depend on water for their solubility in the base materials. The inhibitors of this type which have been tried were not satisfactory either as corrosion inhibitors or as lubricants.

Test results below show the effect obtained when a test fluid is continuously stirred during the flash and fire point determination.

NOTE: The bulk of the water in the fluid has been evaporated before the test is run.

<u>Test Fluid</u>

Polyglycol a	13.5%
Polyglycol b	40.4%
Water	45.0%
Sodium Benzoate	1.0%
Benzotriazole	0.1%

<u>Flash and Fire Points Determined by Cleveland Open Cup Method</u>

	Flash Pt°F			Fire Pt°F		
As reported in the November 27, 1964 Bimonthly Report	I 320	II 280	III 200	I 410	II 640	III 390
Recheck of the same formula		340			570	
The "Cake" and bulk fluid temperatures at the time of the flash and fire pts.	Cake Portion 340		Fluid Portion 500	Cake Portion 570		Fluid Portion 650
Results obtained while continuously stirring		490			625	

Corrosion and Lubricity Studies

Bench stirring corrosion and pump performance tests have served to evaluate selected corrosion inhibitors which have been used as additives to our prototype fire resistant water based hydraulic fluid, Base A.

The stirring corrosion test was used for the bulk screening of materials and to establish minimum effective concentration levels for the inhibitors selected. Those materials which passed the initial screening were further evaluated in a pump test. A vane pump is used to check the lubricity as well as the corrosion preventive properties of the candidate inhibitor materials.

Our use of the procedures is illustrated in the table on page 8. From the stirring corrosion data we see that both Sodium Meta Silicate and Potassium Chromate are effective. However, in the pump test, both materials fail:

(a) Sodium Meta Silicate fails both in corrosion and in its effect on the lubricity of the prototype fluid.

(b) Potassium Chromate fails in its effect on the lubricity of the prototype fluid.

The corrosion information listed is for zinc, the metal most susceptible to attack by Base Fluid A. For the corrosion of other metals evaluated in these tests, see Appendix Tables III and IV.

Test Fluid

Polyglycol a	13.5%
Polyglycol b	39.5 - 41.0%
Water	45.0%
Additives	

Tests Conducted in the Presence of a Zinc Panel (35 Sq. Cm. Surface Area)

Additives	Stirring Corrosion Test* 72 Hrs @ 140°F: Wt Change of Zinc	Stirring Corrosion Test* 72 Hrs @ 140°F: Appearance	Vickers Vane Pump Test* 20 Hrs @ 140°F: Wt Change of Zinc	Vickers Vane Pump Test* 20 Hrs @ 140°F: Appearance	Ring Wear	Vanes Wear
0% Sodium Benzoate 1% Benzotriazole	-41.0 mg	Dull, gray Black Stains at glass contact points or rack	-30.1 mg	White stain and pitting	17 mg	2 mg
05% Sodium Meta licate	+0.5 mg	Clean and bright surface	-54.6 mg	White chalk corrosion and pitting	249 mg	2 mg
3% Potassium omate	+0.4 mg	Clean and bright surface	+2.5 mg	Clean and bright	Extremely high wear after 1 hr. of test	Extremely high wear after 1 hr. of test
			Galvanized steel panel +0.4 mg	Clean and bright		

See Appendix Table II

Status and Future Program

An endurance pump run with a candidate fluid has been set up to test its:

(1) lubricity and stability,

(2) corrosion protection for the several specification metals.

Contamination of the test fluid with up to 10 percent synthetic sea water will be used to demonstrate the effects to be anticipated under service conditions.

A continuing study will be made to evaluate corrosion inhibitor systems which would enhance the properties of our proposed prototype fluid.

The bearing life of the most promising fluids will be determined on an SKF Bearing Test apparatus. The data will then be compared with the results obtained with conventional fluids.

Synthetic work will continue towards developing new materials which will elevate the autoignition temperature of the most promising formula. Corrosion inhibitors, which do not depend on water for their solubility, will be synthesized so that solids formation is eliminated when evaporation of the water has occurred during hydraulic operation.

APPENDIX

APPENDIX TABLE I

Physical Properties of Synthesized Materials

Name	Appearance	Neut No	pH 20% in H_2O	Visc @ 100°F cs	Visc @ 100°F 20% in H_2O cs	RI ND/20°C	Flash Pt. (COC)	Fire Pt. (COC)	AIT°F
PF-450	Reddish liquid- Emulsion forms on shaking	6.7 Base	8.6	-	-	1.5140	-	-	960
HPPE	Reddish liquid	-	8.8	12.9	-	1.5216	220°F	220°F	1000
HPMPE	Reddish brown liquid	2.5 Base	10.0	12.5	insoluble	1.5222	230°F	245°F	965
MB	Water white liquid	6.75	-	-	not insoluble	1.5192	-	-	>950
HPB	Clear, amber fluid	27.3	-	-	-	1.5311	-	-	850
HDEB	Clear, yellow fluid	8.43	-	-	-	1.5180	-	-	<775
HTEB Batch 1	Clear, amber fluid	10.7	2.6	2.98	-	1.5109	-	-	<750
HTEB Batch 2	" "	9.0	-	-	-	1.5155	-	-	780
EDDHPC	Viscous, clear polymer	-	11.6	-	1.76	1.5050	-	-	<775
Treated Poly-glycol a	Very dark fluid	39.2	3.5	153	-	1.4753	340°F	300°F	795
Treated Poly-glycol b	" " "	17.9	3.2	160	-	1.4709	400°F	440°F	775

APPENDIX TABLE II

Corrosion Test Procedures

Stirring C rrosion @ 140°F - modified turbine oil rust test

Metal specimens ar prepared in the same manner as the static liquid phase test - MIL-H-19457 B, Procedure 4.4.4.1. Five specimens are placed in a glass rack which fits into a 400 ml Berzelius beaker of the turbine rust test. The sixth panel is placed beside the rack in the beaker. Three hundred milliliters of fluid are added to the beaker to cover all of the metal specimens and supply a volume of fluid above the rack for stirring. Agitation is supplied by a shortened stirrer paddle which is attached to the drive spindle of the test apparatus. The stem of the paddle is shortened to provide clearance for the rack of specimens immersed on the bottom of the Berzelius beaker. The plastic beaker cover from the rust test apparatus is used also. The stirring speed of 1000 rpm + 50 is maintained during the test and the bath temperature of 140°F is also maintained.

Dynamic Corrosion Test - Reservoir of Vickers vane pump hydraulic circuit - Temperature of test fluid maintained @ 140°F

The panels are prepared by the same procedure as employed in the other tests. After weighing, the specimens in a glass rack are placed in the reservoir of a Vickers 5 GPM hydraulic test circuit which is being used in a lubricity study of the test fluid also. The rack is located in the return side of the reservoir where the test fluid circulates over the panels in turbulent flow.

1.0 NaBz; 0.1 BZT 0.3 NaCr	1.0	0.6	0.6	1.0	0.7	0.9
1.0 NaBz; 0.1 BZT 0.05 NaSi	0.5	0	0.1	-0.2	0.3	-1.5 S
1.0 NaBz; 0.1 BZT 0.3 K Cr	0	0.1	0.1	-0.5 S	-0.5 S	-1.0
1.0 TEABz; 0.1 BZT	- 4.7	- 3.3 S	0.5	-5.2	0.3	0.1
Following run with 10% sea water						
1.0 NaBz; 0.1 BZT 0.05 NaSi	- 1.8	0.3 P	0.7	0.2	0.1	-1.8 S
1.0 NaBz; 0.1 BZT 0.3 NaCr	- 1.7 P	0.5	0.8	0.6	0.8	0.4
1.0 NaBz; 0.1 BZT 0.3 K Cr	- 0.1 S	1.0	1.0	1.0 S	1.0 S	0.8
1.0 TEABz; 0.1 BZT 0.3 K Cr	0.4	2.0 P	0.8	0.4 S	-0.7 S	-0.8 S

NaBz sodium benzoate
BZT benzotriazole
PGB P-glycobor
NaBo borax
TEABz triethanolamine benzoate

NaSi sodium meta silicate
BoH boric acid
NaCr sodium dichromate
K Cr potassium chromate
TEA-Bo triethanolamine borate

APPENDIX TABLE III

<u>Stirring Corrosion Tests</u>

Base Fluid A; 140°F; 72 Hours; 1" x 2" x ¼" Panels
(Weight change in mg; S = stained panel; P - pitting)

Additives (%)	Zinc	Steel	Al	Brass	Bronze	Copper
1.0 NaBz; 0.1 BZT	-41 S	0	0.1	-4.4	+1.3	-1.0
0.5 NaBz: 0.05 BZT	- 8.7 S	-1.6 S	0.1	-1.2	0	1.0
0.5 NaBz	-41.2 S	-18.1 S	0.3 P	-5.7 S	-4.5 S	-3.4 S
1.0 NaBz; 0.1 BZT 2.0 PGB	- 2.8	0.3	0.5 S	-1.0	-1.4	-2.4
0.5 NaBz; 0.05 BZT 1.0 PGB	-33.5 P	0.4	-0.4	0.9	0	-0.3
0.5 NaBz; 0.05 BZT 0.2 NaBo	-39.9 P	0.1	-0.5 S	0.8	0.1 S	-0.1
1.0 NaBz; 0.1 BZT 2 PGB	- 5.2	- 0.1 S	0.2 S	-1.1	0.1	-2.0 S
1.0 NaBz; 0.1 BZT 0.1 NaSi	31.0	3.7	8.2	28.6	3.5	3.3
1.0 NaBz; 0.1 BZT 0.3 BoH	- 9.6 S	0.5 SP	0.2	-1.8	0.6	0.4

APPENDIX TABLE IV

Dynamic Corrosion Tests

Test Conditions: Metal Specimens placed in reservoir of Vickers vane pump hydraulic circuit
Testing Time: 20 Hours Temperature: 140°F
Test Fluids: Polyglycol a - 13.5%; Polyglycol b - 39.5 - 41.0%; Water - 45.0%; Additives

Test Specimens 1" x 2" x ¼"	1.0% Sodium Benzoate 0.1% Benzotriazole		1.0% Sodium Benzoate 0.1% Benzotriazole 0.01% Sodium Meta Silicate		1.0% Sodium Benzoate 0.1% Benzotriazole 0.05% Sodium Meta Silicate	
	Wt Change	Appearance	Wt.Change	Appearance	Wt Change	Appearance
Zinc	-30.1 mg	White stain and pitting	-51.4	Fluid flow pattern shows on panel; also a great deal of pitting	-10.0 mg	White corrosion and pitting
Steel	- 0.4 mg	Clean and bright	+ 5.4 mg	Clean and bright	+ 1.5 mg	Clean and bright
Aluminum	- 0.1 mg	"	+ 4.6 mg	"	+ 0.9 mg	" "
Brass	- 0.9 mg	"	+ 3.8 mg	"	+ 1.0 mg	" "
Bronze	- 0.3 mg	Stained lightly	+ 4.1 mg	Light staining	+ 0.4 mg	" "
Copper	- 0.6 mg	Clean and bright	+ 5.5 mg	Clean and bright	+ 1.7 mg	" "
Zinc*					-54.6 mg*	White corrosion and pitting
Wear of Ring	17 mg		3 mg		249 mg	
Wear of Vanes	2 mg		2 mg		2 mg	

* The second zinc panel was placed in the maximum flow path of the fluid